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Diffusive Mass Transport in Agglomerated Glassy Fallout from a Near-Surface Nuclear Test

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21 0. Abstract

22 Aerodynamic glassy fallout is formed when vapor phase constituents from the nuclear
23 device are incorporated into molten carriers derived from soil or other near-field
24 environmental debris. The effects of speciation and diffusive transport of condensing
25 constituents are not well defined in models of fallout formation. Previously we reported
26 observations of diffuse micrometer scale layers enriched in Na, Fe, Ca, and ^{235}U , and
27 depleted in Al and Ti, at the interfaces of agglomerated fallout objects. Here, we derive
28 the timescales of uranium mass transport in such fallout as it cools from 2500 K to 1500
29 K by applying a 1-dimensional planar diffusion model to the observed $^{235}\text{U}/^{30}\text{Si}$ variation
30 at the interfaces. By modeling the thermal transport between the fireball and the carrier
31 materials, the time of mass transport is calculated to be <0.6 seconds, <1 second, <2
32 seconds, and <3.5 seconds for fireball yields of 0.1 kt, 1 kt, 10 kt, and 100 kt
33 respectively. Based on the calculated times of mass transport, a maximum temperature of
34 deposition of uranium onto the carrier material of ~2200 K is inferred (1σ uncertainty of
35 ~200 K). We also determine that the occurrence of micrometer scale layers of material
36 enriched in relatively volatile Na-species as well as more refractory Ca-species provides
37 evidence for an oxygen-rich fireball based on the vapor pressure of the two species under
38 oxidizing conditions. These results represent the first application of diffusion-based
39 modeling to derive material transport, thermal environments, and oxidation-speciation in
40 near-surface nuclear detonation environments.

41

42 1. Introduction

43 In near-surface nuclear explosions, aerodynamic glassy fallout is produced by the
44 mixing of vaporized device and environmental materials into molten carriers derived
45 from soil and other nearby materials, which quench before coming in contact with the
46 ground (Glasstone and Dolan, 1977). Vaporized materials can either condense directly
47 onto the surface of molten carriers, or can be deposited as already condensed droplets
48 onto the surface of carriers. The condensed material is subsequently mixed into the
49 molten material by diffusion and mechanical mixing (Miller, 1960; Freiling, 1965;
50 Freiling, 1970). The effect of the speciation on condensation and diffusion in fallout
51 materials is poorly understood, but remains fundamental to dispersion models predicting
52 the composition and dispersion of radioactive fallout.

53 Historic fallout formation theories combine physical models with empirical
54 relationships derived from early atmospheric tests (Freiling, 1959; Miller, 1960;
55 Norment, 1979). Refractory species are thought to volumetrically incorporate into carrier
56 materials by mechanical mixing, while volatile species deposit onto the surface of the
57 solidifying carriers. These models consider physical principles such as gas-phase
58 diffusion of species in the fireball, condensation onto and diffusion within carriers, as
59 well as re-evaporation of condensing species under the assumption of equilibrium
60 conditions. Such models do not, however, consider heat transfer from the fireball to the
61 carriers, nor the effect of speciation on condensation and diffusion, both of which affect
62 the rates of condensation onto, and diffusion through, the molten carriers. The potential
63 importance of speciation on the condensation and mixing process is underscored by
64 recent work analyzing the uranium isotopic composition of fallout, which found both
65 inter- and intra-sample heterogeneity (Eppich *et al.*, 2014; Lewis *et al.*, 2015; Weisz *et*

66 *al.*, 2017). In the context of fallout formation models, uranium, if present in an oxide
67 form, may condense first and mix volumetrically into molten carriers due to the
68 refractory nature of uranium oxides (Miller, 1960, Freiling 1965). Stable xenon isotope
69 ratios measured in aerodynamic fallout glass provide evidence that reducing conditions
70 attend at least some phases of fallout formation (Cassata *et al.*, 2014), although recent
71 findings suggest that multiple different oxidation states of U and Fe may be preserved in
72 fallout (Giuli *et al.*, 2010, Pacold *et al.*, 2016). The chemical and isotopic heterogeneity
73 of uranium observed in fallout samples suggests that vapor-phase speciation due to
74 varying redox conditions may be primarily controlled by the amount of air entrained into
75 the fireball, and possibly buffered, to a first order, by the magnitude and speciation of
76 iron present in the vapor phase (Pacold *et al.*, 2016). Clearly, the oxidation state of vapor-
77 phase constituents will impact the condensation and evaporation behaviors in an evolving
78 fireball environment as fallout forms.

79 The interfaces between fused glassy fallout objects can preserve late stage
80 condensation features, including diffusion profiles, (Weisz *et al.*, 2017). In the population
81 of samples studied, these interfaces are characteristically enriched in sodium, iron,
82 calcium, and uranium, and depleted in aluminum and titanium. Similar enrichments of Fe
83 and Ca have been observed in suspected anthropogenic contributions to trinitite glass
84 (Bellucci *et al.*, 2016). The co-location of volatile and refractory elements at the interface
85 implies that after initial condensation, fallout formation continues through a fractionation
86 and diffusion process dictated by the speciation of vapor-phase constituents, and may be
87 affected by contributions from anthropogenic materials (Weisz *et al.*, 2017).

88 Understanding speciation in the vapor phase is essential to establishing a
89 comprehensive model of fallout formation. In this study, we show that the diffuse
90 interfaces observed between agglomerated fallout objects preserve a record of the thermal
91 histories experienced prior to quenching in the fireball. To demonstrate and explore this
92 record, we apply a model of one-dimensional planar diffusion to explain the Gaussian
93 distribution of uranium concentration observed at select agglomerate interfaces.
94 Subsequently, we estimate the time and temperature over which uranium diffusion
95 occurred from this interface. By constraining the time and temperature of mass transport,
96 the deposition temperature of late stage vapor species onto fallout surfaces prior to
97 agglomeration is also constrained. We then use these insights to interpret the source and
98 speciation of vaporized constituents, and the redox conditions of the fireball.

99 2. Modeling methodology and results

100 2.1 Data selection

101 The dataset used for diffusion modeling is derived from agglomerated fallout glasses
102 originating from a uranium-fueled near-surface nuclear test (Weisz *et al.* 2017), and
103 acquired by nano-scale secondary ion mass spectrometry (NanoSIMS). The sample set
104 consists of mm-scale aerodynamic glassy objects with approximately rhyolitic major
105 element compositions. The objects include numerous sub-mm secondary objects fused to
106 the surface of larger glassy objects (Figure 1). Deposition layers at the interfaces of the
107 fused objects were identified using backscatter electron imaging. NanoSIMS ion images
108 were collected at these interfaces showing micro-scale compositional relationships and
109 $^{235}\text{U}/^{30}\text{Si}$ variation (Figure 1).

110 Of the nine interfaces presented in Weisz *et al.* (2017), three of these yielded
111 approximately Gaussian distributions of $^{235}\text{U}/^{30}\text{Si}$ profiles. In the case of a thin layer of
112 condensed species deposited onto the surface of a molten carrier that subsequently fuses
113 with a larger molten object, the deposited layer is expected to diffuse into both objects if
114 there is a chemical potential gradient between the layer and the molten objects. In the
115 idealized case, that the layer comprises a single species, is infinitesimally thin, and is
116 between two homogeneous objects of equal composition. The concentration distribution
117 will evolve from the layer between two objects of equal temperature over time, following
118 the Gaussian form of

$$119 \quad C(x, t) = C_0 e^{\frac{-x^2}{4Dt}} \quad (1)$$

120 where C is concentration, C_0 is the initial concentration of the species in the layer, D is
121 the diffusivity, t is time, and x is the dimension of diffusion (Zhang, 2010). Based on
122 these observations, three approximately Gaussian $^{235}\text{U}/^{30}\text{Si}$ profiles B1, C1, and D2 were
123 chosen as the focus of the diffusive modeling presented, here.

124 The experimentally determined $^{235}\text{U}/^{30}\text{Si}$ ratio profiles at the three chosen interfaces
125 were fit in IGOR Pro software using non-linear least squares regression analysis with a
126 modified Gaussian function:

$$127 \quad G = A + Bx + Cx^2 + \frac{E}{\sigma\sqrt{2\pi}} e^{\frac{-(x-\mu)^2}{2\sigma^2}} \quad (2)$$

128 where σ is the standard deviation of the distribution, μ is the mean of the distribution,
129 E is a fit scaling parameter, and $A+Bx+Cx^2$ is a quadratic expression (with fitting
130 coefficients A , B , and C) added to allow for minor compositional variation on either side
131 of the interface and still acquire a Gaussian fit of the peak. The compositional data at
132 these interfaces were confirmed to approximate Gaussian distributions, and are shown

133 with their modeled fits in Figure 2. Full details on the original samples and analyses, as
134 well as the sample naming scheme, are contained in (Weisz *et al.*, 2017), and the use of
135 the data with our model approach is described, below.

136 2.2 Mass and thermal transport

137 In Figure 3, the interface region is shown to be narrow (<10 micrometers) in
138 comparison to the (mm-scale) host fallout object, indicating that 1-D planar diffusion is
139 an appropriate approximation. Mass transport of uranium at fused fallout interfaces can
140 therefore be approximated using one-dimensional planar diffusion. In the one-
141 dimensional planar diffusion model, the concentration distribution follows the relation

$$142 \quad C(x, t) = C_0 e^{\frac{-x^2}{4Dt}} \quad , \quad (3)$$

143 where C is concentration, C_0 is the initial concentration of the species in the layer, D is
144 the diffusivity, t is time, and x is the dimension of diffusion (Zhang, 2010).

145 Applying the Gaussian form of Equation (3), the standard deviation (σ) from fits of
146 the $^{235}\text{U}/^{30}\text{Si}$ profiles acquired using Equation (2) yields a convolved parameter of
147 average diffusivity and time ($D_{avg}t$) over a given period of mass transport,

$$148 \quad \sigma = \sqrt{2D_{avg}t} \quad , \quad (2)$$

149 where D_{avg} is the average diffusivity over a temperature interval in the medium,
150 presented in Table 1. As diffusivity is temperature dependent according to the Arrhenius
151 equation, we can derive an expression of

$$152 \quad \frac{\sigma^2}{2} = D_{avg}t = \int_{t_1}^{t_2} D_0 e^{\frac{-E_a}{RT(t)}} dt \quad , \quad (3)$$

153 where t_1 is the temperature of initial deposition of material at the interface, t_2 is the
154 temperature at which mass transport effectively stops, $T(t)$ is the cooling rate of the

155 medium, and D_o and E_a are the respective pre-exponential constant and activation energy
156 of the diffusant.

157 The most pertinent parameters of D_o and E_a for uranium diffusion in rhyolitic
158 material in the literature are 363.8 ± 24.0 kJ/mol and $e^{2.51 \pm 0.35}$ cm²/s, respectively (Mungall
159 and Dingwell, 1997). In that study D_o and E_a values were derived as effective binary
160 uranium diffusion parameters determined in a haplogranitic melt (79% SiO₂, 12% Al₂O₃),
161 and assuming uranium to be in the hexavalent state. For our model we also assume
162 uranium in the hexavalent state, as supported by recent work using X-ray absorption near
163 edge structures (XANES) on melt glass from a uranium-fueled test (*i.e.*, UO₂²⁺; Pacold *et*
164 *al.*, 2016).

165 In order to acquire a deposition layer of condensed material at the interface of two
166 fused objects, at least their surfaces were in the liquid state when the layer was deposited
167 and before the objects collided, subsequently solidifying before significant ground
168 interaction. It follows that the cooling rate of the interfaces (where the still molten
169 objects collided) would be controlled by the cooling rate of the fireball. Thus, the
170 cooling rate of the medium (*i.e.*, the molten host object) is considered by computationally
171 modeling thermal transport in a rhyolitic material approximating the shape of two fused
172 spherical fallout objects under cooling fireball conditions using the finite element
173 analysis software, COMSOL (Figure 4). This model simulates two spherical objects that
174 fused together, with the larger object having a diameter of 1.5 mm, and the smaller object
175 having a diameter of 0.4 mm. As shown in the 3-dimensional model, the smaller object
176 is partially embedded in the larger object. In this model, the 'interface' was defined as the
177 outer edge of the larger sphere within the smaller sphere.

178

179 The cooling rate of the fireball was modeled using Hillendahl's equations based on
180 light output curves (Freiling *et al.*, 1965) to provide the yield-dependent fireball cooling
181 rate:

$$182 \quad -\frac{dT}{dt} = 776W^{0.10}t^{-1.34} \cong (3 \times 10^{-11})W^{-0.3}T^4 \quad (4)$$

183 where T is temperature in K, W is the yield in kt, and t is time (in seconds). The fireball
184 cooling rate is then modeled for a range of fireball yields of 0.1 kt, 1 kt, 10 kt, and 100 kt,
185 to generalize results to a range of potential near-surface events.

186 Expanding upon Freiling's 1965 approach, the heat transfer model applied to this
187 system includes conductive, convective, and radiative heat transfer between the fireball
188 and the molten material. Conduction was used to model heat transfer within the molten
189 material, while convective and radiative heat transfer were used to model the external
190 effect of the cooling fireball environment on change in temperature within the modeled
191 fallout object (Fig. 5). The cooling curves at the interface point of the fused objects
192 (Figure 5) were determined for yields of 0.1 kt, 1 kt, 10 kt, and 100 kt from boiling point
193 of SiO₂ (2500 K) to the solidification temperature (1500 K) of fallout glass (Freiling *et al.*,
194 *et al.*, 1965). The cooling curves serve as the input for $T(t)$ in Equation (3). Resultant values
195 for the time that diffusion from the interface effectively stops (t_2) for 0.1, 1, 10, and 100
196 kt yields were calculated to be approximately 3, 4, 8, 10 seconds, respectively. Setting a
197 pre-defined end time (t_2) as the time at which the interface reaches 1500 K (and mass
198 transport effectively stops), we then solved for t_1 , or the time of deposition along the
199 cooling curve for a given yield in the series.

200 2.3 Probability distributions for the time of deposition

201 Using Equation (3), the $D_{avg}t$ parameters (Table 1), in combination with the cooling
 202 equations $T(t)$ for the interfaces at each modeled fireball yield (Fig. 4), enables
 203 determination of the time of deposition t_I for each of interfaces B1, C1, and D2.
 204 However, Equation (3) cannot be analytically solved for deposition time t_I and there are
 205 uncertainties on the values of D_0 , E_a , and $D_{avg}t$. Instead, cumulative probability
 206 distributions for t_I were numerically generated, taking into account these uncertainties,
 207 and subsequently used to determine the model time of deposition t_I and its uncertainty.

208 To generate the cumulative probability distributions for the value of deposition time
 209 t_I , the probability of model success was determined for 100 pre-defined values of t_I
 210 (equal time-steps between $t_I=0$ and $t_I= t_2$, exemplified in Figure 6). The model was
 211 deemed successful if the calculated cooling interval (t_2-t_I) was sufficiently long to
 212 produce the observed diffusion profile, thus satisfying the relation

$$213 \quad \int_{t_1}^{t_2} D_{0U} e^{-\frac{E_a U}{RT(t)}} dt \geq D_{avg}t \quad . \quad (6)$$

214 At each time-step, the probability of model success was determined by generating 1000
 215 randomly selected values from normal distributions of the values of D_0 , E_a , and $D_{avg}t$,
 216 based on their means and uncertainties. Each cumulative distribution function was fit
 217 with an error function, from which the average value (μ_{tI}) and standard deviation (σ_{tI}) of
 218 t_I was determined for the yield-series at each interface. A total of 12 cumulative
 219 distribution functions for the value of t_I were calculated (3 interfaces at 4 different yields;
 220 Table 2).

221 2.4 Temperature of deposition

222 Using the calculated values of μ_{tI} and σ_{tI} , the temperature of deposition T_{dep} was
 223 determined for each interface using the respective cooling curves for each yield (see

224 Table 2). The values for t_l have normally distributed uncertainties (σ = standard
225 deviation); however, because the cooling curves are exponential functions, the
226 uncertainties on T_{dep} simply represent the temperature interval that corresponds to 1σ
227 uncertainty on t_l .

228 The time and temperature of deposition between the interfaces at each corresponding
229 yield show essentially no variation (the values are within 1σ uncertainty). There is,
230 however, substantial relative time variation between each yield in the series, ranging from
231 about 0.5 seconds at 0.1 kt to about 3.4 seconds at 100 kt. This corresponds to a
232 difference in the calculated average temperature of deposition of approximately 150 K
233 between the highest and lowest measured yield for each studied interface.

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237 3 Discussion

238 3.1 The effect of heat transfer between the fireball and the 239 carrier materials

240 Our computational modeling reveals that thermal transport of species in the fireball
241 into molten carrier materials can have a significant effect on the cooling rate used in
242 diffusion modeling (Figure 7). For example, in a 1 kt fireball cooling from 2500 K, a
243 carrier material initially at thermal equilibrium with the fireball will take roughly twice as
244 long to cool 1500 K in comparison to the average fireball temperature. This difference in

245 cooling rate not only affects estimates of mass transport, but also the calculated
246 temperature of late stage deposition of bomb vapor species onto molten fallout objects.

247 While historical fallout formation theories such as by Miller (1960) and Freiling
248 (1965) model interdependent, physicochemical phenomena such as condensation,
249 fractionation, and incorporation of radionuclides, they do not consider heat transfer
250 between the fireball and the carrier materials. Freiling *et al.* (1965) specifically describe
251 effects of mass transport in a cooling fireball environment, including diffusion and re-
252 evaporation from the surface. Both are temperature-dependent processes that control the
253 composition of resultant fallout. Thus, any first-principles fallout formation model must
254 take into account the effect of thermal transport on temperature-dependent mass transport
255 into molten carrier materials.

256 Mass transport and the efficacy of this mechanism for introducing bomb vapor into
257 carrier materials is also dependent on the condensation temperature and the diffusivity of
258 individual species in the vapor. As diffusion is controlled both by thermal and chemical
259 gradients, the Gaussian profiles selected for 1-D diffusion modeling indicate that, at the
260 time of collision of the small droplet and large droplet, the temperature and compositional
261 difference between these two objects was negligible, at least near their respective
262 surfaces. Considering a scenario where both objects were approximately the same
263 composition and temperature, species enriched at the interface would diffuse at the same
264 rate into either object, forming a symmetrical profile. We conclude that these samples,
265 characterized by symmetrical interfaces and similar $D_{avg}t$ values (Table 2), were likely at
266 similar temperatures prior to collision, and did not experience significant re-evaporation
267 from the surface.

268 From this limited sample set that similarly sized fallout objects may have experienced
269 different time-temperature histories prior to quenching. The consistency in the widths of
270 the $^{235}\text{U}/^{30}\text{Si}$ distributions at the interfaces targeted in this study, however, suggests the
271 thermal conditions of deposition of material at the interface and subsequent mass
272 transport into the carriers were similar .By selecting interfaces with Gaussian
273 concentration distributions, indicating that host and agglomerated object boundaries were
274 at similar temperature at the time of collision, we limit the sensitivity of our diffusive
275 modeling to temperature heterogeneities in the fireball.

276 3.2 Constraining the timescale of mass transport and 277 temperature of deposition

278 Through diffusion modeling, we estimate the time of mass transport from the
279 observed deposition layers (Δt) of 2 seconds, 3 seconds, 4.5, and 7 seconds for the 0.1 kt,
280 1 kt, 10 kt, and 100 kt yield models, respectively. These values are comparable to glassy
281 fallout cooling estimates by Bonamici *et al.*, (2017) in objects of similar dimension from
282 the Trinity test. In that study, however, cooling timescales were acquired from diffusive
283 modeling of Si between different compositional phases within trinitite samples, without
284 taking into consideration heat transfer between the fireball and the molten objects. Given
285 that our study focuses on mass transport at sample surfaces, surface-closure times of <3
286 seconds calculated by Cassata *et al.* (2014) may be more directly relevant. These
287 overlapping timeframes of mass transport strongly suggest that incorporation of fission
288 products, unfissioned device materials, and other vaporized constituents into
289 aerodynamic glassy fallout objects occurs over the course of a few seconds. Cassata *et al.*
290 (2014) posit two possible scenarios explaining this rapid closure time: either the location

291 in the fireball where the fallout formed cooled to 1500 K within ~3 seconds, or the
292 molten fallout precursors were ejected from the fireball and rapidly quenched within ~3
293 seconds. The cooling times modeled for each yield series is consistent with average
294 fireball temperatures reaching quenching temperatures within seconds, but does not
295 preclude quenching upon ejection.

296 Modeling a range of yields not only enables generalization of mass transport
297 timescales in a variety of potential nuclear event scenarios, but also bounds the maximum
298 temperatures of deposition. The temperatures of deposition for each hypothetical yield
299 (Fig. 9) were fit by linear least squares regression for each interface, and show a
300 maximum average temperature of deposition of $2185 \pm_{167}^{206}$ K.

301 The temperature of deposition derived from modeling of the data increases inversely
302 with hypothetical yield (Table 2 and Fig. 9). This observation is not unexpected, as the
303 fireball cooling rates are yield-dependent (See Electronic Annex 1, section EA1.3)
304 Correspondingly, in order to acquire the same diffusion profile as a function of increasing
305 yield, the temperature at the time of deposition would have to be higher. Within the
306 resolution of current measurements, however, this effect is minimal. These data show that
307 the determined temperature of deposition does not vary significantly as a function of
308 fireball yield. Specifically, for each of the modeled interfaces, the average temperature of
309 deposition changes by only ~150 K between the 0.1 kt and 100 kt models (Table 2),
310 representing 4 orders of magnitude variation of modeled yield (Fig. 9).

311 3.2 Speciation of vaporized constituents

312 Fallout formation models assert that refractory species will condense and incorporate
313 into molten carrier materials via mechanical mixing or diffusion, whereas volatile species

314 deposit at lower temperatures onto the surface of already quenched carrier materials
315 (Miller, 1960). The interfaces of agglomerated fallout objects preserve characteristic co-
316 located enrichments of some refractory species (*i.e.*, calcium, iron, uranium) and
317 depletion in others (*i.e.*, aluminum and titanium), indicating a co-deposition of Ca, Fe,
318 and U species (Weisz *et al.*, 2017, Table 3). The refractory oxide species, FeO and CaO,
319 are likely derived in part from the local soil as well as from additional anthropogenic
320 sources (Weisz *et al.*, 2017). Both vaporize at around 3000K (Cornell and Schwertmann,
321 2003; Patnaik, 2003). Uranium observed in these samples is dominated by contributions
322 from the device, as evident from the relatively high ²³⁵U enrichment observed (*ibid.*).
323 Uranium metal and UO₂ are generally even more refractory, with boiling points of 4000
324 K and 3800 K, respectively (IAEA, 2008). The maximum calculated temperature of
325 deposition (T_{dep} ; Table 2) has a lower temperature than the boiling point for species of
326 element observed to be enriched at the interface, as well oxides present in the soil that
327 were found to be depleted at the interface (*e.g.*, Al₂O₃). All the aforementioned species
328 (FeO, CaO, U, UO₂, and Al₂O₃) are expected to behave as refractory species and
329 condense out of the vapor phase at higher temperatures. The observed enrichment and
330 depletion behavior at agglomerated fallout interfaces is therefore puzzling.

331 Using the calculated deposition temperature of ~2200 K from our diffusive modeling,
332 we can now interpret the condensation behavior of species enriched or depleted at fallout
333 interfaces (as observed in Weisz *et al.*, 2017) based on temperature-dependent vapor-
334 pressure relationships. The vapor pressure of Al-species in oxidizing (atmospheric)
335 conditions is roughly two orders of magnitude lower than for the Ca-species at ~2200 K,
336 but approximately the same under reducing conditions at that temperature (Lamoreaux *et*

337 *al.*, 1987). Al_2O_3 has a much higher average concentration compared to CaO in soils
338 presumed to be the primary precursor source material (Table 3). If any significant amount
339 of soil was vaporized in the nuclear event, a higher concentration of Al-species in the
340 fireball vapor would be expected in either oxidizing or reducing conditions, and thus, a
341 higher partial pressure based on Raoult's law. In order for an excess of Ca to be present at
342 the interface relative to Al at the calculated deposition temperature (~ 2200 K), a source of
343 Ca in addition to from vaporized soil must have been present (such as a cement structure)
344 to increase the concentration of Ca-species in the vapor. Such an addition would
345 subsequently increase the partial pressure of Ca-species, relative to Al-species prior to
346 formation of the interfaces, and could result in the observed enrichments. For example,
347 rough estimates of the amount concrete needed to produce the excess Ca observed at the
348 interface suggest a concrete to soil ratio of approximately 1:14 (see Electronic Annex 2,
349 based on estimates of vaporized soil from Izrael, 2002) could explain these observations.
350 Multivariate statistical approaches assessing the spatial relationships in major element
351 species (*e.g.*, see Fitzgerald *et al.*, in press) may be used to test this hypothesis in future
352 studies.

353 The co-location of Na_2O (relatively volatile, Walter and Giutronich, 1967) with
354 refractory material at agglomerated fallout interfaces is at odds with current
355 understanding of the relative volatilities of species present in the fireball after a near-
356 surface nuclear event. Assuming equilibrium conditions at ~ 2200 K, the vapor pressure
357 of CaO is expected to be more than 7 orders of magnitude lower than Na (the constituent
358 with the highest vapor pressure of the Na-oxide species) in an oxygen-rich environment
359 (Lamoreaux *et al.*, 1984; Lamoreaux *et al.*, 1987). In a reducing environment, the vapor

360 pressure of Ca (the constituent with the highest vapor pressure in reducing environments)
361 is 11 orders of magnitude lower than Na, even at <1400 K. In either environment, Ca-
362 species and Na-species would be expected to experience relative chemical fractionation,
363 particularly given that Na₂O is more than 2-fold more abundant in the soil than CaO
364 (Eppich *et al.*, 2014). In contrast, in an oxygen-rich environment, the vapor pressure of
365 Na approaches atmospheric pressure at around 2200 K (Lamoreaux *et al.*, 1984). Co-
366 location of Na- and Ca-species would only be possible in an oxygen-rich environment
367 (such as theorized by Adams *et al.*, 1960 and Miller, 1960). This effect would be
368 enhanced in samples such as those studied here if there was substantial contribution of Ca
369 to the vapor from sources other than local soils.

370 The co-location of Na and Ca enrichment bands at object interfaces resulting from
371 oxygenated fireball conditions is in apparent contrast with recent noble gas measurements
372 in fallout. Measurements of Xe precursor volatility indicate that, in some events, the
373 fireball was in a reducing state at the time of system closure (Cassata *et al.*, 2014).
374 However, a recent XANES study of melt glass from near-surface nuclear tests suggests
375 the cooling rate of the fireball (and the carriers entrained in the fireball) can affect the
376 final redox state of the resultant fallout glass (Pacold *et al.*, 2016). It is possible that the
377 incorporation of xenon isotope precursors (the decay products of fission products) into
378 the volume of molten fallout glasses may occur in an earlier, low fO₂ state, while the
379 deposition layers observed in the agglomerated fallout objects in this study are the result
380 of a later stage addition under more oxygenated fireball conditions.

381 While Raoult's law and studies such as those by Lamoreaux *et al.* (1984, 1987) can be
382 used to estimate the vapor pressure and condensation behavior of individual species in a

383 multi-component vapor, these approaches are only applicable to ideal solutions.
384 Interpretation of recent observations in fallout are further complicated when considering
385 the effect of oxidation on a multicomponent vapor, resultant condensates, and
386 multicomponent carrier materials in a high temperature environment. These
387 complications are particularly evident for uranium. Uranium fractionation studies in
388 fallout have reported both refractory and volatile behavior of uranium in post-detonation
389 environments (Moody *et al.*, 2014). Divergent uranium volatility is possibly attributable
390 to the co-existence of multiple species of gaseous uranium in the fireball, each having
391 different thermochemical properties. Species present could include U, UO, UO₂, and
392 UO₃ among others (Grenthe *et al.*, 1992), which have changing, temperature-dependent
393 vapor pressures depending on oxygen fugacity (Rauh *et al.*, 1954). Further, the
394 interaction of uranium with other constituents in a multicomponent vapor could form
395 numerous other complex species, each with a distinct condensation behavior.

396 Such complex behavior is not limited to uranium and oxygen. In vaporization
397 experiments including multiple oxides such as those found in soils (*e.g.*, CaO, MgO,
398 Al₂O₃, TiO₂, and SiO₂), formation of complex gaseous oxides such as CaAlO, CaSiO₃,
399 MgAlO, AlSiO, and CaTiO₃ has also been observed (Shornikov and Yakovlev, 2014).
400 The formation of complex compounds could promote volatility-driven chemical
401 fractionation for some species, and explain why in this study we observe a deposition
402 temperature that is much lower than that predicted based on the boiling points of uranium
403 metal or UO₂, alone (4000 K and 3800 K, respectively). Multicomponent, vapor-phase
404 experiments with controlled oxygen environments will be necessary to determine the
405 extent of this effect, and enable predictive generalization to fallout formation models.

406 4 Conclusions

407 The $^{235}\text{U}/^{30}\text{Si}$ ratio profiles modeled for this study are illustrative of a deposition layer
408 of condensed species onto a molten carrier, and subsequently preserved between two
409 agglomerated, quenched objects. Thermal transport between the fireball and molten
410 carriers can be modeled by applying a one-dimensional diffusive model to compositional
411 interfaces with Gaussian distributions. Results indicate that mass transport from these
412 agglomerate interfaces occurs in less than a few seconds. This process depends on the
413 residence time of the carrier in the fireball, as well the temperatures experienced by the
414 molten carrier material. While these parameters are a function of fireball size to some
415 degree, we find the deposition temperatures to be relatively insensitive to fireball yield.

416 By constraining the duration of mass transport based on diffusion profiles preserved
417 at agglomerated fallout interfaces, we estimate a maximum temperature of deposition of
418 ~ 2200 K. At ~ 2200 K, the observed co-location of Na with Ca (and other, more
419 refractory species such as Fe and U) at some interfaces indicates that the fireball was
420 oxygenated at the time of this surface deposition, prior to agglomeration and quenching.
421 The comparable vapor pressure values for Ca and Al (both depleted at these types of
422 interfaces) suggest that Ca enrichment in these interface layers originated, at least in part,
423 from sources beyond those of vaporized near-field soils.

424 This study demonstrates that micro-scale fallout features preserve useful constraints
425 on fallout formation processes and fireball time-temperature histories. Our observations
426 also imply that oxygen availability in the fireball as a function of time may impact the
427 speciation and relative volatility of vaporized species, and that the degree fireball
428 oxygenation likely changes as a function of time. A more complete understanding of such

429 processes and their effect on resultant fallout compositions may be gained through study
430 of speciation of vaporized constituents under varying oxygen fugacity.

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544

545 7 Tables

546 Table 1

547 Table 2

548 Table 3

549 10. Figures

550 Figure 1. Top left: Optical microscope image of Sample C, a mm-scale
551 aerodynamic fallout glass. Attached, secondary objects are labeled as C1, C2, and C3.
552 Top right: Back-scatter electron (BSE) image of Object C1 attached to Sample C. The
553 interface between the two objects is seen as a bright, diffuse region, indicating higher
554 relative average atomic number in that region. The NanoSIMS isotope ratio image of
555 $^{235}\text{U}/^{30}\text{Si}$ is superimposed over the region where it was acquired at the interface. Bottom
556 left: Isotope ratio image of $^{235}\text{U}/^{30}\text{Si}$ at the interface of Object C1. The region of higher
557 $^{235}\text{U}/^{30}\text{Si}$, indicative of higher ^{235}U concentration, is seen as the white/yellow region,
558 which is co-located with the interface. Bottom right: The $^{235}\text{U}/^{30}\text{Si}$ ratio variation across
559 the interface of Object C1, as acquired from the isotope ratio image along the white arrow
560 (bottom left pane).

561

562 Figure 2. NanoSIMS ion images (left panes) and isotope ratio variation profiles
563 (right panes) across the interface for $^{235}\text{U}/^{30}\text{Si}$ for Objects B1, C1, and D2. The isotope
564 ratio profiles for these interfaces were the ones best fit with a Gaussian distribution out of
565 the sample set, with minimal variation on either side of the interface.

566

567

568 Figure 3. Top: BSE image of the interface between Sample D and Object D2.
569 The interface region is very thin (<5 microns) in comparison to the larger objects.
570 Bottom: Schematic of mass transport from an infinitesimal planar source (red) through a
571 volume (blue) having cross sectional area A, which was used to model deposition layers
572 as shown at Interface D2 (above).

573

574 Figure 4. (A) COMSOL 3-D mockup (see Electronic Annex 1) of aerodynamic
575 fallout glass where two objects have fused together, where the grid scale is in millimeters.
576 The large object is 1.5 mm in diameter, and the smaller attached object is 0.4 mm in

577 diameter. (B) Wire frame of the meshed geometry, using tetrahedra from 1 micron to 100
578 microns, to model the geometry.

579

580 Figure 5. (A) Temperature profile of the 3-D fallout mockup acquired by finite
581 element analysis after 1.0 s of cooling in a 1 kt fireball from 2500 K. This model
582 incorporates conductive and radiative thermal transport with the external environment
583 and within the object. The black arrow indicates the interface point, where the cooling
584 rate equation of the interface was determined for the yield series. (B) Modeled cooling
585 curves for agglomerated fallout interfaces assuming 0.1 kt, 1 kt, 10 kt, and 100 kt yields.

586

587 Figure 6. The cumulative probability distribution function of deposition times for
588 interface B1 is shown in a 1 kt cooling environment. The blue line represents the error
589 function fit of the dataset, which was used to derive uncertainties on the time of
590 deposition (Table 2).

591

592 Figure 7. Modeled interface cooling rate vs. modeled fireball cooling rate, for a 1
593 kt fireball environment. The fireball cools to 1500K in less than 3 seconds, while the
594 interface does not cool to 1500K until 4 seconds have elapsed.

595

596 Figure 8. Left: BSE image of Object C2 attached to Sample C. The $^{235}\text{U}/^{30}\text{Si}$
597 isotope ratio image is shown superimposed over the interface. Middle: The $^{235}\text{U}/^{30}\text{Si}$
598 isotope ratio is shown. The region of high $^{235}\text{U}/^{30}\text{Si}$ ratio is shown skewed towards the
599 larger object, indicative of faster mass-transport into the larger object vs. Object C2.
600 Right: The $^{235}\text{U}/^{30}\text{Si}$ ratio variation profile, as acquired from the isotope ratio image along
601 the white arrow, illustrates this skewing, showing a sharp increase from Object C2 at the
602 interface, and a gradual decrease from the maximum at the interface into the larger object
603 of Sample C.

604

605 Figure 9. Temperature of deposition for each modeled interface vs. the log of the
606 modeled yield, with 1σ uncertainties. The red line is a linear fit, from which the
607 approximate temperature of deposition can be extrapolated for varying yields. While the
608 fit is only applied to the data points, uncertainties in T_{dep} at each yield are systematic
609 (each is dependent on the uncertainties of the diffusivity parameters of uranium). As
610 shown here, the estimated maximum deposition temperature is 2200 K, with maximum
611 1σ uncertainties of ~ 200 K.

612